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ELECTROLYTIC DETERMINATIONS AND SEPARATIONS

THESIS

Presented to the Faculty of the Department of Philosophy of the University of Pennsylvania
For the Degree of Doctor of Philosophy

BY
LILY GAVIT KOLLOCK, A. B.
PHILADELPHIA, PA.

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INTRODUCTION.

That the electric current has greatly aided in the development of new and reliable methods for the determination and separation of metals is no longer questioned. That new material will continue to be added to what we now possess is also certain to occur. But in the old methods, worked out long before correct ideas prevailed as to current density, concentration of the solution and electrode surface, gaps exist, and uncertainty must necessarily prevail in the minds of those who seek to reproduce the proper working conditions of these earlier methods. That the latter are in every sense satisfactory in the hands of those persons who are thoroughly acquainted with them is also beyond question. To render them, however, universally acceptable, and to render their place in analytical chemistry by electrolysis permanent, the absolute conditions for successful work on the part of any investigator, must be definitely established. To this end a number of the earlier methods in which the double cyanides were used as electrolytes have been carefully reviewed in the following pages, and the conditions of current density, amperage, voltage and other factors fully worked out. Thus edited, doubt can no longer be thrown upon the methods proposed, and they will continue to be in their developed condition the most reliable for the purposes for which they have been suggested. They now for accuracy, neatness and rapidity of execution most certainly excel the ordinary gravimetric and volumetric methods applied to the same metals.

It is a pleasure to acknowledge my indebtedness to Professor Edgar F. Smith, at whose suggestion this work was undertaken, and to thank him for his advice, encouragement and kindly interest.

CADMIUM.

In 1878 Smith showed that cadmium could be precipitated quantitatively from its alkaline double cyanide solution. In the following experiments cadmium sulphate containing .1659 gram of cadmium in 10 c. c. was converted into the double cyanide, using, gram of potassium cyanide. The solution was electrolyzed with a current N. D_{100} = 0.04 –0.06 A and V = 2.9–3.2. The solution was heated to 60° C. After the current had passed for six hours, the deposit was washed with hot water and alcohol, dried and then weighed. The solution poured out of the platinum dish, and examined qualitatively for cadmium, showed that all the cadmium had been deposited in this time. It was likewise entirely precipitated when the current was allowed to act on the solution through the night in the cold. The following results were obtained:

RESULTS.

Cadmium.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Metal Found.
gram.	gram.						gram.
0.1659	1	125 c.c.	N. D_{100}=0.06 A.	2.9	57°	7 hours	0.1657
0.1659	1	125 c.c.	N. D_{100}=0.04 A.	2.9	cold	during night	0.1650
0.1659	1	125 c.c.	N. D_{100}=0.06 A.	3.2	60°	3 hours	0.1655

SILVER.

On page 77 of Smith's "Electro-Chemical Analysis" it is stated that silver may be precipitated from a cyanide solution containing an excess of potassium cyanide. It may be deposited with a low current, and has the advantage of non-precipitation of silver peroxide at the anode.

Accordingly a silver nitrate solution containing .1270 gram of silver in 25 c. c., after the addition of 0.5 gram of potassium cyanide, was diluted to 125 c. c. This solution was electrolyzed with a current N. D_{100} = 0.07 A and V = 3.2. The temperature was 65° C. The deposition was complete in three hours. With a current of N. D_{100} = 0.1 A the silver was deposited completely in two hours. The

relation between the current and the time factor may be seen in the following table:

RESULTS.

Silver present.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.					hours.	gram.
0.1270	0.5	100 c.c.	$N.D_{100}=0.07$ A.	3.2	65°	3	0.1271
0.1270	0.5	100 c.c.	$N.D_{100}=0.07$ A.	3.2	65°	3	0.1270
0.1270	0.5	100 c.c.	$N.D_{100}=0.06$ A.	3.2	65°	3	0.1273
0.1270	1	100 c.c.	$N.D_{100}=0.01$ A.	3	65°	2	0.1268
0.1026	1	100 c.c.	$N.D_{100}=0.04$ A.	2.5	65°	5	0.1026
0.1026	1	100 c.c.	$N.D_{100}=0.04$ A.	2.5	65°	5	0.1024

Separations.

SILVER FROM PLATINUM.

In the *American Chemical Journal*, volume xiii, page 417, Smith described this separation. A current of 1 c. c. of oxy-hydrogen gas per minute acted upon a solution of the double cyanide produced by adding 2.5 grams of potassium cyanide. The silver was deposited free from any trace of platinum.

The separation, therefore, was taken up in order to get the exact working conditions. The salts of the metals used were silver nitrate containing .1026 gram of silver, and platinic chloride containing from .0879 gram to .1758 gram of platinum. To the combined solutions 1.25 grams of potassium cyanide were added and the whole diluted to 125 c. c. The current used was N. $D_{100} = 0.04$ A and $V = 2.5$. The temperature was 70°. In from three to four hours the current was interrupted and the deposit washed with hot water and alcohol. It was found to be free from platinum. The filtrate gave no reaction for silver.

RESULTS.

Silver.	Platinum.	Potassium Cyanide.	Current.	Voltage.	Temperature.	Dilution.	Time.	Found.
gram.	gram.	gram.					hours.	gram.
0.1026	0.879	0.5	$N.D_{100}=0.05$ A.	2.5	78°	125 c.c.	5	0.1030
0.1026	0.1758	1.25	$N.D_{100}=0.05$ A.	2.5	75°	125 c.c.	3	0.1022
0.1026	0.1758	1.25	$N.D_{100}=0.45$ A.	2.4	75°	125 c.c.	3	0.1028
0.1026	0.1758	1.25	$N.D_{100}=0.04$ A.	2.5	75°	125 c.c.	3	0 1025
0.1026	0.1758	1.25	$N.D_{100}=0.04$ A.	2.5	75°	125 c.c.	3	0.1025

Silver from Copper.

In the *American Chemical Journal*, volume xi, page 264, there appears a series of forty experiments relating to the separation of these metals. Copper was found to have been precipitated with the silver when the deposition took place from a cyanide solution. It was then thought that copper could not be separated from silver by this method. In 1889 a set of new experiments was reported. By lowering the strength of the current the separation was made. The silver deposit contained no copper nor could silver be detected in the copper solution poured from the dish. In 1895 Smith and Wallace published a report of the separation made in that year.

I found that the following conditions gave accurate results. The solution of silver nitrate used contained .1024 gram of metal and that of copper nitrate contained .0998 gram of copper. To the mixed solution 2 grams of potassium cyanide were added. The liquid containing an excess of potassium cyanide was diluted to 125 c. c. This was subjected to a current of N. D_{100} = 0.03–0.05 A and V = 1.1–1.66. The current acted from three to seven hours. The deposit of silver was free from copper.

The results varied from the theoretical by .0002–.0003 gram.

Results.

Silver.	Copper.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1024	0.0998	2	125 c.c.	N.D_{100}= 0.03 A.	1.16	cold	10	0.1027
0.1024	0.1	2	125 c.c.	N.D_{100}= 0.05 A.	1.1	65°	7	0.1027
0.1024	0.1	1	125 c.c.	N.D_{100}=0.058 A.	1.66	65°	3	0.1026

Silver from Cadmium.

Smith and Spencer (*Journal of American Chemical Society*, Vol. xvi, page 420) found that the deposition of silver

was accelerated by heating the solution during the electrolysis, and that while cadmium may be entirely precipitated in the cold by the current, yet with a low current and a temperature of 60° the cadmium is held in solution. A separation of silver and mercury may be thus effected in a cyanide solution. In the same journal, Smith and Frankel record the separation of mercury from cadmium, zinc, nickel and cobalt. In 1895 Smith and Wallace published later results with the same method. Following the data thus obtained, a solution of silver nitrate containing .1024 gram of silver and cadmium sulphate solution equivalent to .168 gram of cadmium was used. The salts were transformed into their double cyanides by an excess of potassium cyanide. The silver was obtained free from cadmium in four hours. The current used was N. $D_{100} = 0.02$ A and V = 2.15. The temperature was 60° before the current was passed through the solution.

RESULTS.

Silver.	Cadmium.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1024	0.168	2	125 c.c.	N. D_{100}=0.02 A.	2.15	75°	4	0.1025
0.1024	0.168	2	125 c.c.	N. D_{100}=0.02 A.	2.1	60°	4	0.1020
0.1024	0.168	2	125 c.c.	N. D_{100}=0.025 A.	2.15	65°	5	0.1027

The silver in all cases was found free from cadmium.

SILVER FROM ZINC.

These metals were separated according to the following conditions: Using zinc sulphate containing .1 gram of zinc and silver nitrate solution containing .1024 gram of silver. The potassium cyanide used amounted to one gram. The solution was 125 c. c. in volume. It was electrolyzed at 70° by a current of N D_{100} = .032–.038 A and V = 2.76. In three hours the deposition of the silver was complete.

RESULTS.

Silver.	Zinc.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	gram.					hours.	gram.
0.1024	0.1	1	100 c.c.	$N.D_{100}$=0.33 A.	2.76	60°	3	0.1026
0.1024	0.1	1	100 c.c.	$N.D_{100}$=0.38 A.	2.73	70°	3	0.1028
0.1024	0.1	1	100 c.c.	$N.D_{100}$=0.38 A.	2.70	65°	3	0.1027

Nickel and cobalt were separated from silver in a similar way.

SILVER FROM NICKEL.

A solution of nickel nitrate containing .1 gram of nickel was added to a silver nitrate solution and both converted into the double cyanides by 1.5 grams of potassium cyanide. The solution was electrolyzed with a current $N. D_{100} = 0.02 - 0.03$ A and $V = 1.7 - 2$ for three hours. The separation in this time was found to be complete. The results show a variation from the calculated amount of + .0001 gram to — .0002 gram. The solution of silver in nitric acid, when examined qualitatively, gave no evidence of the presence of nickel. The nickel solution, when examined, showed that the silver had been entirely precipitated.

RESULTS.

Silver.	Nickel.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	gram.					hours.	gram.
0.1024	0.1	1.5	125 c.c.	$N.D_{100}$=0.02 A.	1.7	65°	3	0.1026
0.1024	0.1	1.5	125 c.c.	$N.D_{100}$=0.03 A.	2.	65°	5	0.1025
0.1024	0.1	1.5	125 c.c.	$N.D_{100}$=0.03 A.	1.66	60°	3	0.1025

SILVER FROM COBALT.

Cobalt nitrate was the salt used in this separation. To the solution of silver nitrate (.1024 gram if silver) was added a solution of the cobalt salt containing .1 gram of cobalt and 2.75 grams of potassium cyanide. A current of $N. D._{100} = 0.02$ A and $V = 2.2 - 2.7$ at a temperature of 65° was passed through the solution for five hours. The silver in this time was entirely precipitated. No cobalt was found deposited with the silver.

Results.

Silver.	Cobalt.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1024	0.1	2.75	125 c.c.	N. D_{100}=0.038 A.	2.2	65°	5	0.1028
0.1024	0.1	3.5	125 c.c.	N. D_{100}=0.02 A.	2.2	65°	3½	0.1027

Silver from Iron.

Heretofore these metals have not been separated electrolytically in cyanide solution. A solution of ferrous ammonium sulphate, equivalent to 0.1 gram of metallic iron, was treated with sulphurous acid in order to reduce any ferric iron which might exist. After the reduction was complete the excess of acid was nearly neutralized with potassium carbonate. To this 2.5 grams of potassium cyanide were added. The solution of the double cyanide, dark green in color, was added to a solution of silver which had been converted into the double cyanide by 0.5 gram of potassium cyanide. The entire solution was made up to 100 c. c. It was heated to 65° and electrolyzed with a current of N. $D_{100} = 0.04$ A and $V = 2.7$. At the expiration of three hours the silver was found to be entirely deposited. There was in some cases a separation of ferric oxide at the anode. The silver, after its solution in nitric acid, was tested for iron by ammonium sulphocyanide. A faint pink color, due to a trace of iron in the acid used for the solution of the metal, was observed. The deposit, which was light gray in color, varied but slightly from the theoretical amount of the silver present in the solution.

Results.

Silver.	Iron.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1002	0.1	3	125 c.c.	N. D_{100}=0.025 A.	1.8	65°	4	0.1001
0.1002	0.1	2.5	125 c.c.	N. D_{100}=0.02 A.	1.8	70°	4	0.1005
0.1002	0.1	3.25	125 c.c.	N. D_{100}=0.038 A.	2.2	65°	3	0.1000
0.1174	0.1	3	125 c.c.	N. D_{100}=0.04 A.	2.25	70°	3	0.1176
0.1174	0.2	4	125 c.c.	N. D_{100}=0 04 A.	2.2	70°	3	0.1174
0.1174	0.1	3	125 c.c.	N. D_{100}=0.05 A.	2.2	75°	3	0.1175

MERCURY.

In the *American Chemical Journal*, volume xi, page 264, it is recorded that mercury may be separated without difficulty with a low current and a large excess of alkaline cyanide. The deposits are noted as "compact, rather gray in color, and showed in a few cases a drop-like nature so characteristic of mercury." The time required for the deposition under the conditions given was 12–14 hours. Smith and Wallace, in the *Journal of the American Chemical Society*, in 1895, published a number of separations of mercury from other metals—zinc, cadmium, cobalt and nickel. The time required for the separation was reduced to 3 and 3½ hours.

In the experiments made this year the following conditions gave good results and confirmed those previously made. A solution of mercuric chloride, containing .1439 gram of mercury in 10 c. c. and 0.5 gram of potassium cyanide, was diluted to 100 c. c. It was electrolyzed with a current N. $D_{100} = 0.07$ A and V = 3.2. The temperature of the solution was 65° C. In three hours the metal was completely deposited. The deposit was washed with slightly warm water.

RESULTS.

Mercury.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Found.
gram.	gram.					hours.	gram.
0.1439	0.5	100 c.c.	$N.D_{100}$=0.07 A.	3.2	65°	3½	0.1441
0.1439	0.5	100 c.c.	$N.D_{100}$=0.07 A.	3.2	65°	3½	0.1442
0.1439	0.5	100 c.c.	$N.D_{100}$=0.02 A.	1.6	65°	6	0.1440
0.1439	0.5	100 c.c.	$N.D_{100}$=0.07 A.	3.1	65°	3	0.1436

The deposits obtained were light gray in color and were easily washed. They were bright and metallic in appearance, with higher voltage.

Separations.

MERCURY FROM COPPER.

In the *American Chemical Journal*, volume xi, page 264, Smith and Frankel report the separation of mercury and

copper in an alkaline cyanide solution. A current generating 2 c. c. of oxyhydrogen gas per minute was used for this purpose. The solution used contained .1833 gram of mercury and 14–70 per cent of copper were added. With a current generating 3.2 c. c. of oxyhydrogen gas, mercury was completely deposited in sixteen hours. It is stated, however, that when the quantity of copper present exceeded 20 per cent the results were unsatisfactory. Later Smith and McCauly took up the separation again and by careful regulation of the current, were enabled to effect it even when the metals were present in equal quantities.

In repeating this work a solution of mercuric chloride equivalent to .1216 gram of mercury and a copper sulphate solution equivalent to 0.1 gram of copper were used. An excess of potassium cyanide was added. The entire solution was diluted to 125 c. c. The current acting upon the solution was N. $D_{100} = 0.04$ A and $V = 1.09$. The temperature was 65°. In from two to four hours the mercury was completely deposited. On testing the metal qualitatively, the deposit was found free from copper.

RESULTS.

Mercury.	Copper.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Found.
gram.	gram.	grams.					hours.	gram.
0.1216	0.1	2.0	125 c. c.	N. D_{100}=0.02 A.	1.09	cold	16	0.1220
0.1216	0.1	2.5	125 c. c.	N. D_{100}=0.03 A.	1.9	65°	4	0.1216
0.1216	0.15	3.5	125 c. c.	N. D_{100}=0.035 A.	1.8	65°	2½	0.1213
0.1216	0.1	3.0	125 c. c.	N. D_{100}=0.04 A.	1.9	65°	3	0.1215

MERCURY FROM NICKEL.

These metals were separated in an analagous manner to that described under the separation of silver from nickel. To the solutions of mercuric chloride and nickel nitrate were added 2 grams of potassium cyanide. This was then diluted to 125 c. c. A current of N. $D_{100} = 0.04$ A and $V = 2.2$ was allowed to act for three hours. The deposit was found to weigh .0003 gram less than the calculated

amount of mercury present. The filtrate was found to contain no mercury. No nickel was deposited with the metal.

RESULTS.

Mercury.	Nickel.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Found.
gram.	gram.	grams.					hours.	gram.
0.1216	0.1	2	125 c. c.	$N.D_{100}=0.04$ A.	1.7	65°	4	0.1220
0.1216	0.1	2	125 c. c.	$N.D_{100}=0.04$ A.	2.2	65°	4	0.1220
0.1216	0.15	2.5	125 c. c.	$N.D_{100}=0.04$ A.	2.2	65°	4	0.1211
0.1216	1	2	125 c. c.	$N.D_{100}=0.04$ A.	2.2	65°	4	0.1213

MERCURY FROM COBALT.

The mercuric chloride used in this separation contained .1216 gram of mercury and the cobalt nitrate contained 0.1 gram of cobalt. Two grams of potassium cyanide were added to the mixed solutions which were diluted to 100 c. c. The current acting was $N.\ D_{100} = 0.03$ A and $V = 2.9$. With a temperature of 60° the deposition of the mercury was complete in five hours. It was free from cobalt.

RESULTS.

Mercury.	Cobalt.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Deposited.
gram.	gram.	grams.					hours.	gram.
0.1216	0.1	2	100 c.c.	$N.D_{100}=0.025$ A.	2.45	cold	16	0.1217
0.1216	0.1	2	100 c.c.	$N.D_{100}=0.025$ A.	2.06	65°	5	0.1213
0.1158	0.1	2	100 c.c.	$N.D_{100}=0.03$ A.	2.9	65°	5	0.1152

MERCURY FROM ZINC.

The results obtained in the separation of mercury from zinc were first reported by Smith and Frankel in 1889. The electrolysis took place at the ordinary temperature in sixteen hours, with a current generating 3 c. c. of oxyhydrogen gas per minute.

In the experiments made this year the following conditions gave satisfactory results,

RESULTS.

Mercury.	Zinc.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1158	0.1	2	125 c.c.	$N.D_{100}$=0.05 A.	3	60°	4	0.1152
0.1158	0.1	1.5	125 c.c.	$N.D_{100}$=0.033 A.	2.5	50°	4	0 1155
0 1158	0.2	2	125 c.c.	$N.D_{100}$=0.025 A.	2.9	50°	4	0.1155

In the third determination the current acted for three hours at 50° and then all night in the cold. The deposit in all cases was gray and compact. The mercury on examination for zinc gave no reaction for that metal, while no mercury was found in the zinc solution.

MERCURY FROM CADMIUM.

As stated under the separation of silver from cadmium, Smith and Wallace (*Journal of American Chemical Society*, 1895) found that cadmium might be separated from both silver and mercury by keeping the temperature slightly elevated. Unless this precaution is taken cadmium is precipitated with both metals, even when a low current is used.

The following proved to be good working conditions: The mercuric chloride solution used contained .1182 gram of mercury, and the cadmium sulphate solution was equivalent to .2206 gram of cadmium. The double alkaline cyanides were produced by the addition of 2.5 grams of potassium cyanide. A current of $N. D_{100} = .018$ A and V = 1.7 was passed through the solution, previously heated to 65° for seven hours. The mercury deposit was free from cadmium and weighed .1181 gram, which was .0001 gram lighter than the theoretical amount of mercury. It was repeatedly found that when the current was greater than 0.02 A, cadmium was precipitated.

MERCURY FROM PLATINUM.

This separation was first carried out and reported by Smith in the *American Chemical Journal*, volume xiii, p. 417.

The deposit of mercury was effected by using a current generating 2 c. c. of oxyhydrogen gas a minute. The alkaline cyanide used for .1902 gram of mercury was 2.5 grams. According to these suggestions a separation of the two metals was made. The mercury in solution was .1373 gram, and the platinum in the platinic chloride contained from .025 gram to 0.1 gram. In four hours the separation was completed. The current was N. $D_{100} = 0.05$ A and V = 2.1 to 2.3. The results show an error of—.0001 gram to + .0003 gram.

RESULTS.

Mercury.	Platinum.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Deposited.
gram.	gram.	grams.					hours.	gram.
0.1373	0.025	3	125 c. c.	N. D_{100}=0.05 A.	2.12	65°	4	0.1372
0.1373	0.01	3	125 c. c.	N. D_{100}=0.04 A.	2.12	75°	4	0.1376
0.1373	0.01	3	125 c. 3.	N. D_{100}=0.045 A.	2.12	70°	4	0.1375

MERCURY FROM IRON.

The separation of mercury from iron, like that of silver from iron, has not been previously attempted in alkaline cyanide solution. Accordingly the following method was developed and found to yield satisfactory results:

The solution of the cyanide of iron was prepared from ferrous ammonium sulphate in precisely the same way as that described in the separation of silver from iron. The mercuric chloride solution contained .1216 gram of mercury. The cyanide present was from 1 gram to 3 grams, and the current was N. $D_{100} = 0.05$ A and V = 2.5. The temperature during the electrolysis was maintained at 70° C. In three hours the mercury was completely deposited. It was free from iron. The mercury deposit was dissolved in concentrated nitric acid. After diluting a few crystals of ammonium sulphocyanide were added. A faint pink color was observed, which was found to be due to the small trace of iron in the nitric acid.

RESULTS.

Mercury.	Iron.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Deposited.
gram.	grams.	grams					hours .	gram.
0.1216	0.1	1	100 c.c.	$ND._{100}$=0.05 A.	2.	70°	3	0.1215
0.1216	0.3	3	100 c.c.	$ND._{100}$=0.04 A.	2.	70°	4	0.1217
0.1216	2.5	2.5	100 c.c.	$ND._{100}$=0.02 A.	2.7	65°	4	0.1217

GOLD SEPARATIONS.

In the *American Chemical Journal*, volume xiii, Smith and Muhr report the separation of gold from palladium, platinum, zinc, cobalt, nickel and copper.

GOLD FROM PALLADIUM.

It has been previously shown that palladium is not deposited with a current of .01 A in the presence of an excess of potassium cyanide. With a current liberating .8 c. c. of oxyhydrogen gas a minute, and the solution containing 1.5 grams of potassium cyanide, .1162 gram of gold was deposited in from twelve to fourteen hours.

In accordance with this suggestion, the following conditions were obtained: Two grams of potassium cyanide were added to a solution of gold chloride containing .1256 gram of metal and palladium chloride equivalent to .1 gram of metallic palladium. This was diluted to 250 c. c. The current used was N. D_{175} = 0.06–0.09 A and V = 2.5. The temperature during the decomposition was 65°. In five hours the current was raised to 0.09 A. The gold was found to be completely deposited and free from palladium.

RESULTS.

Gold.	Palladium.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1256	0.1	2	125 c. c.	N.D_{100}=0.06–0.03 A.	2.5	65°	6	0.1250
0.1256	0.1	2	250 c. c.	N.D_{175} 0.06–0.09 A.	2.5	65°	6	0.1257

Gold from Copper.

In the report referred to, the separation of gold from copper in cyanide solution took place with a current liberating .8 c. c. of oxyhydrogen gas at the ordinary temperature in about twelve hours.

It was found that by heating the solution to 65° the precipitation was more rapid, but required more cyanide in order to keep the copper from being deposited with the gold. To a solution of gold chloride containing .1665 gram of metallic gold and copper sulphate containing 0.1 gram of copper were added 4 grams of potassium cyanide. The solution (250 c. c.), warmed to 65°, was electrolyzed with a current of N. D_{175} = 0.05–0.07 A and V = 1.7—for two and one-half hours. In this time .1667 gram of gold was obtained. There was no reaction for copper when the deposit treated with nitric acid was tested for that metal.

Results.

Gold.	Copper.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1665	1	2	250 c. c.	N D_{175} .07 A.	1.7	65°	2½	0.1667
0.1627	1	2	250 c. c.	N. D_{175}=0.05–0.08 A.	1.9	65°	3	0.1627

Gold from Nickel.

The conditions under which this separation is made are similar to those obtained *under* the separations of silver and mercury from nickel. The solution of gold chloride used was equivalent to .1610 gram of metallic gold, and nickel nitrate contained 0.1 gram of nickel. They were converted into their double cyanides by the addition of 4 grams of potassium cyanide. A current of N. D_{100} = 0.05 A and V = 1.5 was passed through the solution (125 c. c.) at 60° for six hours. The gold on examination contained no nickel.

RESULTS.

Gold.	Nickel.	Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1567	0.1	4	125 c.c.	$N.D._{100}$=0.05 A.	1.7	65°	7	0.1567
0.1610	0.1	4	125 c.c.	$N.D._{100}$=0.05 A.	1.5	60°	7	0.1603

GOLD FROM COBALT.

More difficulty was experienced with the separation of these metals than with the preceding. Four grams of potassium cyanide were added to the solution of gold chloride and cobalt nitrate equivalent to 0.1 gram of cobalt. The current used for the deposition of the gold was N. D_{100} = 0.05 A and V = 1.7. The electrolysis was carried out at 60° C. It was found advantageous before the end to add 1 c. c. of a 20 per cent sodium hydrate solution and raise the current to 0.08 A in order to deposit the last trace of gold. In this way the gold was entirely deposited in seven hours free from cobalt.

RESULTS.

Gold.	Cobalt.	Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Dilution.	Time.	Gold Found.
gram.	gram.	grams						hours.	gram.
0.1610	0.1	4	125 c. c.	$N.D_{100}$=0.05–0.08 A.	1.7	60°	125 c. c.	6¾	0.1612
0.1610	0.1	4	125 c. c.	$N.D_{100}$=0.05–0.08 A.	1.7	60°	125 c. c.	6	0.1608
0.1495	0.1	4	250 c. c.	$N.D_{175}$=0.05–0.08	1.7–2	60°	250 c. c.	6	0.1497

GOLD FROM ZINC.

These metals were successfully separated according to the following conditions: Four grams of potassium cyanide were added to a solution of gold chloride and zinc sulphate containing 0.1 gram of zinc. The current acting upon the double cyanides was N. D_{100} = 0.06 A and V = 2.66. The temperature of the solution was 60°. In seven hours the deposition was complete. No zinc was found with the gold.

Results.

Gold.	Zinc.	Cyanide.	Current.	Voltage.	Dilution.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1495	0.1	4	$N.D_{100}$=0.06 A.	2.66	125 c. c.	60°	7	0.1490
0.1608	1.	4	$N.D_{175}$=0.06 A	2.7	250 c. c.	65°	7	0.1602

Gold from Platinum.

To the solution of gold chloride containing .1576 gram of gold and platinic chloride equivalent to .125 gram of platinum, were added 1.5 grams of potassium cyanide. The volume of the solution was 250 c. c. A current of N. D_{175} = 0.01 A and V = 2.7 was used. The temperature was 70° C. In three hours the gold was entirely precipitated. No platinum was deposited with the gold. The deposit weighed .1479 gram.

Mercury from an Alkaline Sulphide Solution.

In 1891 Smith made the statement that mercury obtained as mercuric sulphide, during analysis may be accurately estimated electrolytically. The sulphide was dissolved in sodium sulphide of sp. gr. 1.19 and electrolyzed with a current generating 1 c. c. of oxyhydrogen gas per minute, acting during the night. The mercury was always compact and gray in color.

In working out conditions for the determination of mercury by this method, 25 c. c. of sodium sulphide were added to a solution of mercuric chloride containing .1403 gram of mercury. This solution, diluted to 125 c. c., was electrolyzed at 70° C by a current of N. D_{100} = 0.11 A and V = 2.5. In five hours the mercury was entirely deposited. It was light gray in color. Slightly warm water was used in washing the deposit.

RESULTS.

Mercury.	Sodium Sulphide, Sp. gr. 1.19	Dilution.	Current.	Voltage.	Temperature.	Time.	Mercury Found.	Error.
gram.						hours.	gram.	gram.
0.1403	25 c. c.	100 c. c.	N. D_{100}=0.11 A.	2.5	70°	5	0.1400	0.0003
0.1403	25 c. c.	100 c. c.	N. D_{100}=0.12 A.	2.7	70°	5	0.1404	0.0001

COPPER.

"Moore advises dissolving the recently precipitated copper sulphide obtained during the ordinary course of analysis in potassium cyanide, and after the addition of an excess of ammonium carbonate, electrolyze the warm (70°) solution." —*Electro-Chemical Analysis*, Smith, page 61. According to this suggestion the following conditions for the determination of copper were found to give good results: The copper sulphate solution used contained .1270 gram of metallic copper. This was precipitated as sulphide, which was dissolved in 2 grams of potassium cyanide and ammonium carbonate added. The solution, diluted to 125 c. c., was heated to 70° C. and electrolyzed with a current of N. D_{100} = 0.02–0.07 A and V = 4. In three hours the copper was completely deposited. The copper was found to weigh .1269 gram, that is .0001 gram less than the theoretical amount.

COPPER FROM NITRIC ACID SOLUTION.

Copper has also been successfully determined electrolytically in a nitric acid solution (*American Chemical Journal*, Vol. xii, p. 329). A solution containing 10 c. c. of concentrated nitric acid was diluted to 100 c. c. and electrolyzed. The current used was N. D_{100} = 0.03 A and V = 1.7. At the ordinary temperature in sixteen hours .1396 gram of copper was precipitated. The solution treated with ammonium hydroxide showed that the copper had been entirely deposited. With a temperature of 65° and a current of N. D_{100} = 0.09 A and V = 1.9 in five hours .1397 gram of copper was found, and another deter-

mination under identical conditions gave the theoretical amount of copper present.

RESULTS.

Copper.	Nitric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Copper Found.
gram.						hours.	gram.
0.1398	10 c.c.	100 c.c.	$N.D_{100}=0.03$ A.	1.7	cold	16	0.1396
0.1398	10 c.c.	100 c.c.	$N.D_{100}=0.09$ A.	1.9	70°	16	0.1397
0.1398	10 c.c.	100 c.c.	$N.D_{100}=0.09$	1.9	65°	16	0.1398

CADMIUM FROM SULPHURIC ACID SOLUTION.

In the *American Chemical Journal*, volume ii, page 42, Smith describes the quantitative deposition of cadmium from its sulphuric acid solution. Cadmium oxide was dissolved in sulphuric acid. The solution contained 2 c. c. of free sulphuric acid of sp. gr. 1.095.

The volume of the solution was 25 c. c. In two hours the cadmium was completely precipitated. The amount of cadmium present was .0931 gram. The following conditions were found to give good results by this method. A solution of cadmium sulphate containing .1599 gram of metal after adding 3 c. c. of sulphuric acid sp. gr. 1.09 and diluting to 125 c. c. was electrolyzed with a current of $N. D_{100} = 0.078$ A and $V = 2.61$. The temperature during the electrolysis was 65°. In five hours the deposition of cadmium was complete. The metal weighed .1604 gram.

BISMUTH.

Smith and Thomas deposited bismuth from a citrate solution which contained an excess of sodium citrate (*American Chemical Journal*, Vol. v, p. 114). Bismuth hydrate was dissolved in citric acid and sodium hydrate added to alkaline reaction. In Smith's *Electro-Chemical Analysis*, page 69, it is stated that bismuth may be precipitated from an alkaline citrate solution, and a solution containing free citric acid. The conditions under which the deposition took place are not recorded. The following

experiments were accordingly made in order to obtain the proper working conditions:

Bismuth from an Ammonium Citrate Solution.

A bismuth nitrate solution was made, adding sufficient nitric acid to the salt to prevent the formation of a basic nitrate on the addition of water. To a solution of this salt containing .1882 gram of metallic bismuth were added 3 grams of citric acid and the solution made ammoniacal. It was diluted to 125 c. c. The temperature was raised to 70° C. A current of N. $D_{100} = 0.02$ A and $V = 1.8$ was allowed to act for three hours. At the expiration of this time the current was increased to N. $D_{100} = 0.04$ A and $V = 2.3$. Finally, in order to deposit the last traces of the metal held in solution the current was made N. $D_{100} = 0.09$ A. The deposit of bismuth obtained in this way was light gray in color, very compact and adherent. In one case the current acted all night and the deposit was darker in color, but adherent and easily washed. There was a noticeable amount of the peroxide of bismuth deposited. The anode was weighed therefore before and after the electrolysis and from the weight of the bismuth peroxide found the amount of the bismuth deposited in this way calculated and added to the weight of that precipitated upon the kathode.

Results.

Bismuth.	Citric acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.	grams.					hours.	gram.
0.1882	3	125 c. c.	N. D_{100}=0.02 (for 3 hours).	1.8	70°	16	0.1881
			N. D_{100}=0.04 A.	2.3	all night in cold.		
			N. D_{100}=0.06 A.				
0.1882	3	125 c. c.	N. D_{100}=0.02 A (for 3 hours).	1.6	70°	6¾	0.1880
			N. D_{100}=0.04 A.	2			
			N. D_{100}=0.09 A.	3			
0.1882	3	125 c. c.	N. D_{100}=0.03 A.	2	65°	6	0.1819
			N. D_{100}=0.042 A.	2.58			
			N. D_{100}=0.09 A.	3			
0.1822	3	125 c. c.	N. D_{100}=0.03 A.	2	65°	6	0.1820
			N. D_{100}=0.042 A.	2.6			
			N. D_{100}=0.09 A.	3			

Bismuth from a Potassium Citrate Solution.

The solution of bismuth nitrate used contained .1777 gram. To this were added 7 grams of citric acid, followed by an excess of potassium hydrate. The solution was diluted to 125 c. c. The temperature was 70°. The current for this solution was also low at the beginning and was gradually increased to 0.09 A. The deposit of bismuth peroxide on the anode was treated as indicated in the preceding method. The bismuth was in all cases a gray, compact, adherent deposit.

Results.

Bismuth.	Citric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.	grams.					hours.	gram.
0.1767	7	125 c.c.	$N.D_{100}$=0.02 A. $N.D_{100}$=0.038 A.	2.16 2.18	65°	5	0.17648
0.1777	7	125 c.c.	$N.D_{100}$=0.02 A. $N.D_{100}$=0.05 A.	2.5 3	70°	5	0.1781
0.1777	7	125 c.c.	$N.D_{100}$=0.03 A. $N.D_{100}$=0.05 A.	2.1 2.5	65°	5½	0.1774

Bismuth from a Citric Acid Solution.

Seven grams of citric acid were added to a solution of bismuth nitrate containing .1767 gram of bismuth. The solution at 70° was electrolyzed with a current N. D_{100} = 0.02 A and V = 1.8. Subsequently it was increased to N. D_{100} = 0.07 A and V = 2.6.

Results.

Bismuth.	Citric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.	grams.					hours.	gram.
0.1767	7	125 c. c.	$N.D_{100}$=0.02 A. $N.D_{100}$=0.038 A.	1.8 2.6	65°	5	0.17648
0.1767	5	125 c. c.	$N.D_{100}$=0.02 A. $N.D_{100}$=0.05 A.	1.8 2.66	70°	5	0.1761

Mercury from Nitric Acid Solution.

The fact that mercury could be determined satisfactorily from a nitric acid solution appears in the *Berichte der deutschen Gesellshaft*, 19, 329. Mercuric nitrate was electrolyzed

by Smith and Knerr (*American Chemical Journal*, volume viii, page 206). There was 0.5–1 c. c. of free nitric acid present. Bright, shining deposits of .0911 gram were obtained in thirty minutes. The current used for the purpose liberated 4 c. c. of oxyhydrogen gas per minute.

In the following work 3 c. c. of concentrated nitric acid were added to a solution of mercuric chloride containing .1403 gram of metallic mercury. The solution (125 c. c.) was electrolyzed with a current N. $D_{100} = 0.06$ A and V = 2 for four hours. The temperature was 70° C. The solution in the dish was siphoned off before the interruption of the current.

RESULTS.

Mercury.	Nitric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.						hours.	gram.
0.1403	3 c.c.	125 c.c.	N. D_{100}=0.06 A.	2	70°	4¼	0.1404
0.1403	3 c.c.	125 c.c.	N. D_{100}=0.07 A.	1.91	70°	4	0.1406

MERCURY FROM SULPHURIC ACID SOLUTION.

It has been known that mercury could be deposited from a solution feebly acidulated with sulphuric acid for a considerable time. The current which was used generated 5–6 c. c. of oxyhydrogen gas per minute. In repeating this method for the precipitation of mercury 1 c. c. of sulphuric acid was added to a solution of mercuric chloride. A current of N. $D_{100} = 0.4$–0.6 A and V = 3.5 effected the deposition. The temperature during the operation was 65° C. The mercury was entirely deposited in one hour. It had a brilliant metallic appearance. It was washed with cold water. The mercury present in the solution was .1403 gram. The deposit weighed .1402 gram.

IRON FROM A CITRATE SOLUTION.

In 1888 Smith reported the deposition of iron from a sodium citrate solution containing free citric acid. The

solution used was ferric ammonium sulphate, and the current acting upon the solution gave 6 c. c. of oxyhydrogen gas per minute.

The method was repeated, using a solution of the alum containing .0378 gram of metallic iron, 10 c. c. of sodium citrate, equivalent to 1.18 grams and 3 c. c. of citric acid equivalent to .059 gram, and the solution diluted to 125 c. c. With a current of N. $D_{100} = .58$ A and $V = 5.7$ in seven hours the deposition was complete. Another determination gave .0375 gram of iron, and a third gave .0379 gram. By titration with potassium permanganate the deposit was found to contain .03789 gram of iron. The carbon, therefore, in this deposit was .079 per cent.

Similar experiments were conducted, using .1035 gram of iron. The current used was N. $D_{175} = 0.8$ A and $V = 9$. The temperature was 60° during the electrolysis. The solution was 250 c. c. The deposit weighed .1046 gram. By titration of the iron 1.06 per cent of C. was found. With identical conditions, using .1280 gram of iron, .94 per cent of C. was found in the deposited metal.

Results.

Iron.	Citrate.	Citric Acid.	Current.	Voltage.	Temperature.	Time.	Found.	Carbon, PerCent
gram.	grams.	gram.				hours.	gram.	
0.0378	10 c. c.=1.18	3 c. c.=.059	N. D_{100}=0.58 A.	5.7	35°	7	0.0379	0.079
0.0378	10 c. c.=1.18	3 c. c.=.059	N. D_{175}=8-1.3	9-11	70°	4	0.0383	1.1
0.1035	10 c. c.=1.18	3 c. c.=.059	N. D_{175}=8	9-11	50°	4½	0.1046	1.06
0.1277	10 c. c.=1.18	5 c. c.	N. D_{100}=0.4-1.A.	7-11	50°	4½	0.1278	
0.1277	10 c. c.=1.18	5 c. c.	N. D_{100}=.8 A	7-8	50°	4½	0.1280	0.94